

Rigid rotators and diatomic molecules via Tsallis statistics

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Abstract

We obtain an analytic expression for the specific heat of a system of N rigid rotators exactly in the high temperature limit, and via a perturbative approach in the low temperature limit. We then evaluate the specific heat of a diatomic gas with both translational and rotational degrees of freedom, and conclude that there is a mixing between the translational and rotational degrees of freedom in nonextensive statistics.

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I Introduction

The nonextensive generalization of Boltzmann-Gibbs statistics was proposed by Tsallis [1] to study systems involving long-range interactions, long-range microscopic memory, and nonequilibrium phenomenon. The nonextensive statistics has been applied in a wide range of areas like self-gravitating systems [2, 3, 4], solar neutrinos [5, 6], and biological systems [7, 8]. The functional form of the generalized entropy reads

$$S_q = k \left[\frac{W^{1-q} - 1}{1 - q} \right] \equiv k \ln_q W, \quad q \in \mathbb{R}_+, \quad (1.1)$$

where k is a constant generalizing the Boltzmann constant k_B for an arbitrary q , and W is the weight factor. In the $q \rightarrow 1$ limit the Tsallis entropy S_q reduces to the standard Boltzmann-Gibbs entropy S . It is interesting to observe that these two entropies may be interrelated via hypergeometric functions as

$$S/k_B = {}_2F_1(1, 1; 2; -(1-q)S_q/k) S_q/k, \quad (1.2)$$

$$S_q/k = {}_1F_1(1; 2; (1-q)S/k_B) S/k_B. \quad (1.3)$$

Based on the entropy (1.1) a canonical formulation was developed in [9, 10]. As a concrete example of using this formalism for studies of various statistical systems at equilibrium the classical monoatomic ideal gas has been investigated as a N -body problem [11, 12] in detail, and, in particular, the specific heat of this system has been computed exactly.

In the above context study of the rigid rotator has been initiated in [13, 14]. Using molecular dynamics a numerical study of N rotators with a long-range interaction has been done in [13], where a long-standing metastable state with anomalous duration suggesting nonextensivity has been observed. In [14] an analytical study of the rigid and non-rigid rotators has been done. These authors, however, obtained the specific heat of the system by studying a single rigid rotator. In the regime of nonextensive statistics, strictly speaking, the study of a single rigid rotator cannot be extended to a system of N rigid rotators as it is familiarly done in the extensive Boltzmann-Gibbs scenario. A systematic study of statistics of N rigid rotators is, therefore, essential for understanding the dependence of the specific heat on the temperature. We will comment on the other relevant issues in appropriate places.

In the present work we first evaluate the specific heat at the high temperature limit for N rigid rotators, and a diatomic gas endowed with both translational and rotational degrees of freedom. Towards this end we construct an implicit equation involving the generalized partition function and the internal energy. In the high temperature limit the implicit equation is solved *exactly* and explicit expression for the specific heat is evaluated. Contrarily, obtaining an exact solution of the said implicit equation for a system of N rigid rotators in the low temperature limit appears to be difficult. We, therefore, use the method developed in [10] that interrelates the ensemble probabilities obtained via the second and the third constraint approaches, respectively, after performing a suitable transformation on the temperature. This transformation connects the second constraint approach [9] that utilizes unnormalized q -expectation values to the third constraint [10] approach based on the normalized q -expectation values. To construct the pertinent transformation here we

adopt a perturbative approach by disentangling the q -exponential in an infinite series of ordinary exponential [15], and retain terms upto the order $(1 - q)^2$. In the context of the gas of N diatomic molecules we notice that a mixing of the translational and rotational degrees of freedom in the nonextensive terms occur for the specific heat. We here assume a large mass for the diatomic molecules so that their vibratory motions may be neglected. The plan of the paper is as follows. The specific heat of N rigid rotators in the high and low temperature regimes are discussed in Sections II and III, respectively. This is followed by our discussions on the specific heat of a diatomic gas in Sec. IV. Our concluding remarks are given in Sec. V.

II Rigid rotators in the high temperature limit

The energy eigenvalues of an ensemble of N isotropic rigid rotators read

$$E = \frac{\hbar^2}{2I} \sum_{i=1}^N l_i(l_i + 1), \quad l_i = 0, 1, \dots, \quad (2.1)$$

where I is the moment of inertia of a rotator. The generalized partition function of a canonical ensemble of N rotators at an inverse temperature $\beta = 1/kT$ in the third constraint framework [10] is given by

$$\bar{Z}_q^{(3)}(\beta) = \sum_{l_i=0}^{\infty} \mathcal{D} \left[1 - (1 - q) \frac{\hat{\beta}}{c} (\mathcal{L} - \Omega_R U_q) \right]^{\frac{1}{1-q}}, \quad c = \sum_i [p_i^{(3)}(\beta)]^q, \quad (2.2)$$

where $\Omega_R = 2I/\hbar^2$, $\hat{\beta} = \beta/\Omega_R$. The degeneracy factor \mathcal{D} and the sum \mathcal{L} read

$$\mathcal{D} = \prod_{i=1}^N (2l_i + 1), \quad \mathcal{L} = \sum_{i=1}^N l_i(l_i + 1). \quad (2.3)$$

In the expression (2.2) the ensemble probability in the third constraint approach is given by

$$p_i^{(3)}(\beta) = \left[1 - (1 - q) \frac{\hat{\beta}}{c} (\mathcal{L} - \Omega_R U_q) \right]^{\frac{1}{1-q}} (\bar{Z}_q^{(3)}(\beta))^{-1}. \quad (2.4)$$

At high temperature limit the rotational levels are closely spaced, and, therefore, the sum in (2.2) is well-approximated by an integral

$$[\bar{Z}_q^{(3)}(\beta)] = \int_{l_i=0}^{\infty} \mathcal{D} \left[1 - (1 - q) \frac{\hat{\beta}}{c} (\mathcal{L} - \Omega_R U_q) \right]^{\frac{1}{1-q}} \prod_{i=1}^N dl_i. \quad (2.5)$$

The integral may be exactly evaluated as

$$\bar{Z}_q^{(3)}(\beta) = c^N \left[\exp_q \left(\frac{\beta}{c} U_q^{(3)} \right) \right]^{\Lambda(1)} \Phi \hat{\beta}^{-N}, \quad \Phi = \prod_{n=1}^N [1 + (1 - q)n]^{-1}, \quad (2.6)$$

where $\Lambda_{(k)} = 1 + k(1 - q)N$. As a consequence of the property [10]

$$c = [\bar{Z}_q^{(3)}(\beta)]^{(1-q)}. \quad (2.7)$$

the above expression of the generalized partition function may be regarded as an implicit equation. The internal energy of the system introduced via the escort probabilities [10]

$$U_q^{(3)} = \frac{\sum_i E_i (p_i^{(3)})^q}{\sum_i (p_i^{(3)})^q} \quad (2.8)$$

may be recast in the following form:

$$U_q^{(3)} = \frac{1}{\Omega_R \bar{Z}_q^{(3)}(\beta)} \int_{l_i=0}^{\infty} \mathcal{L} \mathcal{D} \left[1 - (1 - q) \frac{\hat{\beta}}{c} (\mathcal{L} - \Omega_R U_q) \right]^{\frac{q}{1-q}} \prod_{i=1}^N dl_i. \quad (2.9)$$

Parallel to (2.5) the above integral may be completed, and this, in turn, produces an implicit equation for the internal energy:

$$U_q^{(3)} = \frac{N c^{N+1}}{\beta \bar{Z}_q^{(3)}(\beta)} \Phi \left[\exp_q \left(\frac{\beta}{c} U_q^{(3)} \right) \right]^{\Lambda_{(1)}} \hat{\beta}^{-N}. \quad (2.10)$$

Substituting (2.6) in (2.10) the internal energy is found to be proportional to the trace c :

$$U_q^{(3)} = c N \beta^{-1}. \quad (2.11)$$

Employing (2.5), (2.7) and (2.11) we obtain an explicit expression for the generalized partition function:

$$\bar{Z}_q^{(3)}(\beta) = [\exp_q(N)]^{\mu_1} \Phi^{\mathfrak{L}_{(1)}} \hat{\beta}^{-N \mathfrak{L}_{(1)}}, \quad \mathfrak{L}_{(k)} = \Lambda_{(-k)}^{-1}, \quad \mu_k = \Lambda_{(k)} \mathfrak{L}_{(k)}. \quad (2.12)$$

The structure of Φ given in (2.6) makes it evident that the generalized partition function (2.12) for N rotators has singularities at the values of q given by $q = (n + 1)/n$ for $n = 1, 2, \dots, N$. The number of singularities equals the number of degrees of freedom of the system. As the number of rotators N increases the singularities tend to accumulate at $q = 1$, the limiting value where the statistical mechanics becomes extensive. The generalized partition function is, therefore, well-defined in the interval $0 < q < 1 + 1/N$, where the upper limit is characterized by the total number of the rotators. The above discussion makes it apparent that in the context of nonextensive thermodynamics the size N of the system is of key importance in selecting the admissible range of the nonextensivity parameter q . In contrast to our result the authors of Ref. [14] considered the generalized partition function at the high temperature limit for the parameter range $1 < q < 2$. Employing the results (2.7), (2.11) and (2.12) the internal energy

$$U_q^{(3)}(\beta) = \frac{N}{\beta} \Lambda_{(1)}^{\mu_1} \Phi^{(1-q)\mathfrak{L}_{(1)}} \hat{\beta}^{(q-1)N \mathfrak{L}_{(1)}}. \quad (2.13)$$

and the specific heat of the system may be computed:

$$C_q^{(3)} \equiv \frac{\partial U_q^{(3)}}{\partial T} = N k \mathfrak{L}_{(1)} \Phi^{(1-q)\mathfrak{L}_{(1)}} \Lambda_{(1)}^{\mu_1} \hat{\beta}^{(q-1)N \mathfrak{L}_{(1)}}. \quad (2.14)$$

The specific heat of the rigid rotators in the high temperature limit, in contrast to its classical value, becomes a temperature dependent quantity for nonextensive statistics. In the extensive $q \rightarrow 1$ limit we recover the classical Boltzmann-Gibbs statistics for these thermodynamics quantities: $U_q \rightarrow N k_B T$, $C_q \rightarrow N k_B$.

To obtain the internal energy (2.13) and the specific heat (2.14) we may also employ the method discussed in [10], where the physical quantities evaluated in the second constraint approach are transformed to those in the third constraint approach by introducing a fictitious temperature β' that is useful for calculation. The ensemble probabilities in the second constraint and the third constraint approaches are now linked as

$$p^{(3)}(\beta) = p^{(2)}(\beta'). \quad (2.15)$$

In other words, the second constraint approach is employed as a convenient tool at the intermediate stages of calculation, and finally results are translated to the third constraint approach via certain transformations. The general transformation rule for the temperature reads

$$\beta = \beta' \frac{\sum_i [p_i^{(2)}(\beta')]^q}{1 - \frac{(1-q)\beta' U_q^{(2)}(\beta')}{\sum_i [p_i^{(2)}(\beta')]^q}} \quad (2.16)$$

In the present example of the rigid rotators at the high temperature limit this relation assumes the form

$$\frac{1}{\beta'} = \left[\Omega_R^{(1-q)} \Phi^{(1-q)} \Lambda_{(N)}^2 \right]^{\mathfrak{L}_{(1)}} \left(\frac{1}{\beta} \right)^{\mathfrak{L}_{(1)}}. \quad (2.17)$$

The specific heat and the internal energy evaluated using this technique is identical to the results (2.13) and (2.14) where the third constraint method has been used *ab initio*.

III Rigid rotators in the low temperature limit

In the example of N rigid rotators at the low temperature limit we obtain the thermodynamic quantities perturbatively by treating $(1-q)$ as the series parameter. This process involves use of the second constraint approach as an intermediate step. The results corresponding to the third constraint approach are then extracted [10] via transformations (2.15) and (2.16) linking the ensemble probabilities in these two approaches. The partition function of N rigid rotator in the second constraint setting reads

$$Z_q^{(2)}(\beta) \equiv Tr \exp_q(-\hat{\beta} \mathcal{L}) = \sum_{l_i=0}^{\infty} \mathcal{D} [1 - (1-q)\hat{\beta} \mathcal{L}]^{\frac{1}{1-q}}, \quad \exp_q(\mathcal{X}) = (1 + (1-q) \mathcal{X})^{\frac{1}{1-q}} \quad (3.1)$$

and the pertinent ensemble probability is given by

$$p^{(2)}(\beta) = [1 - (1-q)\hat{\beta} \mathcal{L}]^{\frac{1}{1-q}} (Z_q^{(2)}(\beta))^{-1}. \quad (3.2)$$

In the low temperature regime the $l_i = 0$ and $l_i = 1$ quantum levels generate the dominant contribution to the partition function.

Using an infinite product expansion of the q -exponential [15]

$$\exp_q(-\hat{\beta}\mathcal{L}) = \exp\left(-\sum_{k=1}^{\infty} \frac{(1-q)^{k-1}}{k} \hat{\beta}^k \mathcal{L}^k\right) \quad (3.3)$$

we express the partition function (3.1) as a perturbative series in $(1-q)$, and retain terms upto second order:

$$Z_q^{(2)}(\beta) = \sum_{l_i=0,1} \mathcal{D} \left[1 - (1-q) \frac{\hat{\beta}^2}{2} \mathcal{L}^2 + (1-q)^2 \left(\frac{\hat{\beta}^4}{8} \mathcal{L}^4 - \frac{\hat{\beta}^3}{3} \mathcal{L}^3 \right) \right] \exp(-\hat{\beta}\mathcal{L}). \quad (3.4)$$

Recasting the above series as

$$Z_q^{(2)}(\beta) = \left[1 - (1-q) \frac{\hat{\beta}^2}{2} \frac{\partial^2}{\partial \hat{\beta}^2} + (1-q)^2 \left(\frac{\hat{\beta}^3}{3} \frac{\partial^3}{\partial \hat{\beta}^3} + \frac{\hat{\beta}^4}{8} \frac{\partial^4}{\partial \hat{\beta}^4} \right) \right] \sum_{l_i=0,1} \mathcal{D} \exp(-\hat{\beta}\mathcal{L}) \quad (3.5)$$

we obtain the series expansion

$$Z_q^{(2)}(\beta) = [f(\beta)]^N [1 - (1-q)\mathcal{F}_1 + (1-q)^2(\mathcal{F}_2 + \mathcal{F}_3 + \mathcal{F}_4 + \mathcal{F}_5)], \quad (3.6)$$

where the coefficients read

$$\begin{aligned} \mathcal{F}_1 &= 6N\hat{\beta}^2 \mathcal{E}(\beta) + 18N(N-1)\hat{\beta}^2 [\mathcal{E}(\beta)]^2, \\ \mathcal{F}_2 &= (6N\hat{\beta}^4 - 8N\hat{\beta}^3)\mathcal{E}(\beta), \\ \mathcal{F}_3 &= (126N(N-1)\hat{\beta}^4 - 72N(N-1)\hat{\beta}^3)[\mathcal{E}(\beta)]^2, \\ \mathcal{F}_4 &= (324N(N-1)(N-2)\hat{\beta}^4 - 72N(N-1)(N-2)\hat{\beta}^3)[\mathcal{E}(\beta)]^3, \\ \mathcal{F}_5 &= 162N(N-1)(N-2)(N-3)\hat{\beta}^4[\mathcal{E}(\beta)]^4, \\ \mathcal{E}(\beta) &= \exp(-2\hat{\beta})[f(\beta)]^{-1}, \quad f(\beta) = 1 + 3\exp(-2\hat{\beta}). \end{aligned} \quad (3.7)$$

The defining property of the internal energy in the second constraint framework

$$U_q^{(2)}(\beta) = -\frac{\partial}{\partial \beta} \ln_q Z_q^{(2)}(\beta) \quad (3.8)$$

and the series (3.6) allows us to extract the perturbative result

$$U_q^{(2)}(\beta) = \mathcal{G}_1 + (1-q)(\mathcal{G}_2 + \mathcal{G}_3 + \mathcal{G}_4), \quad (3.9)$$

where the coefficients may be listed as

$$\begin{aligned} \mathcal{G}_1 &= \frac{6}{\Omega_R} N \mathcal{E}(\beta), \quad \mathcal{G}_2 = \left(\frac{6N^2}{\Omega_R} \ln f(\beta) + \frac{12N\beta}{\Omega_R^2} - \frac{12N\beta^2}{\Omega_R^3} \right) \mathcal{E}(\beta), \\ \mathcal{G}_3 &= \left(\frac{36N\beta^2}{\Omega_R} + \frac{36N(N-1)\beta}{\Omega_R^2} - \frac{72N(N-1)\beta^2}{\Omega_R^3} \right) [\mathcal{E}(\beta)]^2, \\ \mathcal{G}_4 &= \frac{216N(N-1)\beta^2}{\Omega_R^3} [\mathcal{E}(\beta)]^3. \end{aligned}$$

The thermodynamic quantities in the third constraint scenario materialize on transforming $\beta \rightarrow \beta'$ *à la* (2.16). The key quantity κ enacting this transformation may be factorized as

$$\kappa \equiv \sum_i (p_i^{(2)})^q = \chi(\beta) (Z_q^{(2)}(\beta))^{-q}, \quad \chi(\beta) = \sum_{l_i=0,1} \mathcal{D}[1 - (1-q)\hat{\beta}\mathcal{L}]^{q/1-q}. \quad (3.10)$$

In the present case we evaluate the sum $\chi(\beta)$ perturbatively and retain terms upto order $(1-q)^2$. Recasting as a differential series

$$\begin{aligned} \chi(\beta) = & \left[1 - (1-q) \left(\hat{\beta} \frac{\partial}{\partial \hat{\beta}} - \frac{\hat{\beta}^2}{2} \frac{\partial^2}{\partial \hat{\beta}^2} \right) \right. \\ & \left. + (1-q)^2 \left(\hat{\beta}^2 \frac{\partial^2}{\partial \hat{\beta}^2} + \frac{5\hat{\beta}^3}{6} \frac{\partial^3}{\partial \hat{\beta}^3} + \frac{\hat{\beta}^4}{8} \frac{\partial^4}{\partial \hat{\beta}^4} \right) \right] \sum_{l_i=0,1} \mathcal{D} \exp(-\hat{\beta}\mathcal{L}), \end{aligned} \quad (3.11)$$

we obtain $\chi(\beta)$ as

$$\begin{aligned} \chi(\beta) = & Z_q^{(2)}(\beta) + [f(\beta)]^N [(1-q)6N \hat{\beta}\mathcal{E}(\beta) + (1-q)^2 12N\{(\hat{\beta}^2 - \hat{\beta}^3)\mathcal{E}(\beta) \\ & + 3(N-1)(\hat{\beta}^2 - 3\hat{\beta}^3)[\mathcal{E}(\beta)]^2 - 9(N-1)(N-2)\hat{\beta}^3[\mathcal{E}(\beta)]^3\}]. \end{aligned} \quad (3.12)$$

The relations (3.10), (3.12) and the partition function (3.6) now yield κ upto the order $(1-q)^2$:

$$\kappa = 1 + (1-q)\mathcal{P}_1 + (1-q)^2(\mathcal{P}_2 + \mathcal{P}_3 + \mathcal{P}_4), \quad (3.13)$$

where the coefficients read

$$\begin{aligned} \mathcal{P}_1 &= N \ln f(\beta) + 6N\hat{\beta} \mathcal{E}(\beta), \\ \mathcal{P}_2 &= \frac{N^2}{2} [\ln f(\beta)]^2 + (6N\hat{\beta}^2 - 12N\hat{\beta}^3 + 6N^2\hat{\beta} \ln f(\beta)) \mathcal{E}(\beta), \\ \mathcal{P}_3 &= (18N(N-1)\hat{\beta}^2 + (108N - 72N^2)\hat{\beta}^3)[\mathcal{E}(\beta)]^2, \\ \mathcal{P}_4 &= 216N(N-1)\hat{\beta}^3[\mathcal{E}(\beta)]^3. \end{aligned} \quad (3.14)$$

The transformation (2.16) may now be produced as a perturbative series:

$$\beta = \beta' + (1-q) \beta' g(\beta') + (1-q)^2 \beta' h(\beta'), \quad (3.15)$$

where the coefficients read

$$\begin{aligned} g(\beta') &= N \ln f(\beta') + 12N\hat{\beta}' \mathcal{E}(\beta'), \\ h(\beta') &= 432N(N-1)\hat{\beta}'^2 [\mathcal{E}(\beta')]^3 + 18N\hat{\beta}'^2 (5N - 3 + (12 - 8N)\hat{\beta}') [\mathcal{E}(\beta')]^2 \\ &\quad + 6N(3\hat{\beta}'^2 - 4\hat{\beta}' + N\hat{\beta}') \mathcal{E}(\beta') + \frac{N^2}{2} [\ln f(\beta')]^2. \end{aligned} \quad (3.16)$$

To proceed with our computation, we, however, need to invert the series (3.15). This, upto the order $(1-q)^2$ is given as

$$\beta' = \beta [1 - (1-q) g(\beta) + (1-q)^2 (\beta g(\beta) g'(\beta) + [g(\beta)]^2 - h(\beta))]. \quad (3.17)$$

Insofar as the transformation $\beta \rightarrow \beta'$ a temperature dependent process we can not use the *same* construction of the transformation in the *distinct* regimes of high and low temperatures. This was, however, done in the earlier work on the rigid rotator [14]. On this we disagree with them.

Employing the key properties (2.7) and (2.15) we now extract the generalized partition function in the setting of the third constraint:

$$[\bar{Z}_q^{(3)}(\beta)]^{(1-q)} = \kappa + (1-q)^2 12N^2 \hat{\beta}^2 [12\hat{\beta}\mathcal{E}(\beta) + \ln f(\beta)] \{\mathcal{E}(\beta) - 3[\mathcal{E}(\beta)]^2\}. \quad (3.18)$$

The defining thermodynamic relationships

$$\beta \frac{\partial U_q}{\partial \beta} = \frac{\partial \ln_q \bar{Z}_q^{(3)}}{\partial \beta}, \quad (3.19)$$

$$C_q^{(3)} = -k\beta \frac{\partial \ln_q \bar{Z}_q^{(3)}}{\partial \beta} \quad (3.20)$$

now allow us to produce the specific heat at the low temperature limit in the context of the third constraint:

$$C_q^{(3)} = \mathcal{C}_{BG} - (1-q)[\mathcal{C}_1 + \mathcal{C}_2 + \mathcal{C}_3 + \mathcal{C}_4], \quad (3.21)$$

where the familiar classical Boltzmann-Gibbs extensive term \mathcal{C}_{BG} reads

$$\mathcal{C}_{BG} = 12Nk\hat{\beta}^2 \mathcal{E}(\beta) - 36Nk\hat{\beta}^2 [\mathcal{E}(\beta)]^2.$$

The nonextensive terms in (3.21) at the order of $(1-q)$ are listed below:

$$\begin{aligned} \mathcal{C}_1 &= 12Nk[N(\hat{\beta}^2 - 2\hat{\beta}^3) \ln f(\beta) + \hat{\beta}^2 - 4\hat{\beta}^3 + 2\hat{\beta}^4] \mathcal{E}(\beta), \\ \mathcal{C}_2 &= 36Nk[N \ln f(\beta)(6\hat{\beta}^3 - \hat{\beta}^2) + (12 + 2N)\hat{\beta}^3 - (14 + 8N)\hat{\beta}^4] [\mathcal{E}(\beta)]^2, \\ \mathcal{C}_3 &= 216Nk[\hat{\beta}^3 + 2\hat{\beta}^3 \ln f(\beta) + (10N - 12)\hat{\beta}^4 - 4\hat{\beta}^3] [\mathcal{E}(\beta)]^3, \\ \mathcal{C}_4 &= -3888N(N+1)k \hat{\beta}^4 [\mathcal{E}(\beta)]^4. \end{aligned} \quad (3.22)$$

In the classical $q \rightarrow 1$ limit the specific heat (3.21) of N rotators reduces, expectedly, to its Boltzmann-Gibbs value. In the $N = 1$ rotator case, we, unfortunately, fail to notice this occurring in [14].

At the low temperature limit the leading term in internal energy may now be computed via integrations in (3.20). We quote the result:

$$U_q^{(3)} = \mathcal{U}_{BG} + (1-q) (\mathcal{U}_1 + \mathcal{U}_2 + \mathcal{U}_3 + \mathcal{U}_4 + \mathcal{U}_5), \quad (3.23)$$

where the coefficients read

$$\begin{aligned} \mathcal{U}_{BG} &= 6N\Omega_R \exp(-2\hat{\beta}) [1 - 3\exp(-2\hat{\beta}) + 6\exp(-4\hat{\beta})], \\ \mathcal{U}_1 &= 12N\Omega_R \exp(-2\hat{\beta}) [\hat{\beta} - \hat{\beta}^2], \\ \mathcal{U}_2 &= N\Omega_R \exp(-4\hat{\beta}) [1 + 36(N-2)\hat{\beta} + 18(8N+1)\hat{\beta}^2], \\ \mathcal{U}_3 &= 2N\Omega_R \exp(-6\hat{\beta}) [(2-N) + (11-20N)6\hat{\beta} - (12+21)18\hat{\beta}], \\ \mathcal{U}_4 &= \frac{81N\Omega_R}{8} \exp(-8\hat{\beta}) [(6N+3/2) + (14N+3/2)\hat{\beta} + (36N+42)\hat{\beta}^2], \\ \mathcal{U}_5 &= \frac{2916N\Omega_R}{125} \exp(-10\hat{\beta}) [(1+10\hat{\beta})(9N+4) - 200(N+1)\hat{\beta}^2]. \end{aligned} \quad (3.24)$$

IV Gas molecules with translational and rotational degrees of freedom

Physically another aspect of nonextensivity may be of interest. Most often systems incorporate multiple degrees of freedom. In the nonextensive scenario this may indicate that the thermodynamic quantities such as specific heat are likely to have temperature dependent terms of mixed origin. These terms are generated due to the *coexistence* of different degrees of freedom. Another way of visualizing this is that nonextensivity of statistics induces effective interaction terms between two separate components of the microscopic Hamiltonian of the system. In contrast to this, different degrees of freedom remain disjoint in the usual extensive statistical mechanics. As a prototype of this idea we consider here an ideal diatomic gas endowed with both the translational and the rotational degree of freedom. For the purpose of simplification we assume the molecules to be of large mass so that we may disregard the vibrational modes. We also restrict our considerations here to the high temperature limit.

The energy of a diatomic molecule is given by

$$\epsilon = \sum_{i=1}^3 \frac{p_i^2}{2m} + \frac{\hbar^2}{2I} l(l+1), \quad l = 0, 1, \dots \quad (4.1)$$

The generalized partition function in the third constraint is given by

$$\bar{Z}_q^{(3)} = \frac{1}{N! h^{3N}} \sum_{l_i=0}^{\infty} \mathcal{D} \int_{-\infty}^{\infty} \left[1 - (1-q) \frac{\beta}{c} \left(\frac{P^2}{2m} + \frac{\mathcal{L}}{\Omega_R} - U_q \right) \right]^{\frac{1}{1-q}} \prod_{i=1}^N d^3 q_i d^3 p_i, \quad (4.2)$$

where $P^2 = \sum_i p_i^2$. Following Sec. II, here also we, in the high temperature limit, replace the summation on the rotational levels by an integral:

$$\bar{Z}_q^{(3)} = \mathcal{V} \int_{l_i=0}^{\infty} \int_{p_i=-\infty}^{\infty} \mathcal{D} \left[1 - (1-q) \frac{\beta}{c} \left(\frac{P^2}{2m} + \frac{\mathcal{L}}{\Omega_R} - U_q \right) \right]^{\frac{1}{1-q}} \prod_{i=1}^N dl_i d^3 p_i, \quad (4.3)$$

where the numerical factor reads $\mathcal{V} = V^N / N! h^{3N}$. The partition function may now be exactly evaluated as

$$\bar{Z}_q^{(3)} = \mathcal{V} c^{5N/2} (1-q)^{-5N/2} \left[\exp_q \left(\frac{\beta}{c} U_q^{(3)} \right) \right]^{\Lambda_{(5/2)}} \mathbf{G} \hat{\beta}^{-N} \check{\beta}^{-3N/2}, \quad (4.4)$$

where \mathbf{G} is a ratio of two gamma functions and $\check{\beta}$ is a scaled temperature:

$$\mathbf{G} = \Gamma \left(\frac{2-q}{1-q} \right) \left(\Gamma \left(\frac{2-q}{1-q} + \frac{5N}{2} \right) \right)^{-1}, \quad \check{\beta} = \frac{\beta}{2\pi m}. \quad (4.5)$$

A similar evaluation of the internal energy leads us to

$$U_q^{(3)}(\beta) = \frac{5N}{2} \frac{\mathcal{V} c^{\frac{5N}{2}+1}}{\beta \bar{Z}_q^{(3)}} (1-q)^{-5N/2} \left[\exp_q \left(\frac{\beta}{c} U_q^{(3)} \right) \right]^{\Lambda_{(5/2)}} \mathbf{G} \hat{\beta}^{-N} \check{\beta}^{-3N/2}. \quad (4.6)$$

Fortunately the ratio of two implicit equations (4.4) and (4.6) assumes a simple form

$$U_q^{(3)} = \frac{5Nc}{2\beta}. \quad (4.7)$$

On substituting (4.7) in (4.4) and (4.6) we evaluate the generalized partition function and the internal energy explicitly:

$$\begin{aligned} \bar{Z}_q^{(3)} &= \Psi [\exp_q(5N/2)]^{\mu_{5/2}} \hat{\beta}^{-N\mathfrak{L}_{(5/2)}} \check{\beta}^{-\frac{3N}{2}\mathfrak{L}_{(5/2)}}, \\ U_q^{(3)}(\beta) &= \frac{5N}{2\beta} \Psi^{(1-q)} \Lambda_{(5/2)}^{\mu_{5/2}} \hat{\beta}^{(q-1)N\mathfrak{L}_{(5/2)}} \check{\beta}^{(q-1)\frac{3N}{2}\mathfrak{L}_{(5/2)}}, \\ \Psi &= [\mathcal{V} (1-q)^{-\frac{5N}{2}} \mathbf{G}]^{\mathfrak{L}_{(1)}}. \end{aligned} \quad (4.8)$$

The specific heat of the diatomic gas in the high temperature limit is directly produced via the internal energy in (4.8)

$$C_q^{(3)}(\beta) \equiv \frac{\partial}{\partial T} U_q^{(3)}(\beta) = \frac{5Nk}{2} \mathfrak{L}_{(5/2)} \Lambda_{(5/2)}^{\mu_{5/2}} \Psi^{\mathfrak{L}_{(5/2)}} \check{\beta}^{(q-1)\frac{3N}{2}\mathfrak{L}_{(5/2)}} \hat{\beta}^{(q-1)N\mathfrak{L}_{(5/2)}}. \quad (4.9)$$

The above specific heat of the diatomic gas can also be verified by employing the $\beta \rightarrow \beta'$ transformation procedure discussed and used in Sec. III. The relevant transform in the present case is quoted below:

$$\frac{1}{\beta'} = \left[\mathcal{V} \Omega_T^{3N/2} \Omega_R^N \mathbf{G} (1-q)^{-5N/2} \right]^{(1-q)\mathfrak{L}_{(5/2)}} \Lambda^{2\mathfrak{L}_{(5/2)}} \left[\frac{1}{\beta} \right]^{\mathfrak{L}_{(5/2)}}. \quad (4.10)$$

Expanding the specific heat (4.9) of the gas molecules having both translational and rotational degrees of freedom in the parameter $(1-q)$, we retain terms upto the order of $(1-q)^2$:

$$C_d = \frac{5N}{2}k \left[1 + (1-q)\Xi_d + (1-q)^2 \left(\frac{\Xi_d^2}{2} + \frac{5N}{2}\Xi_d - \frac{25N^2}{8} - \frac{5N}{4} \right) \right], \quad (4.11)$$

where $\Xi_d = \ln \mathcal{V} - (3N/2) \ln \check{\beta} - N \ln \hat{\beta} + 5N$. For the purpose of comparison we now consider an expansion of the translational specific heat [11] in the parameter $(1-q)$ while retaining terms upto order $(1-q)^2$:

$$C_t = \frac{3N}{2}k \left[1 + (1-q)\Xi_t + (1-q)^2 \left(\frac{\Xi_t^2}{2} + \frac{3N}{2}\Xi_t - \frac{9N^2}{8} - \frac{3N}{4} \right) \right], \quad (4.12)$$

where $\Xi_t = \ln \mathcal{V} - (3N/2) \ln \check{\beta} + 3N$. Applying the same expansion in the rotational specific heat in the high temperature case (2.14), we obtain

$$C_r = Nk \left[1 + (1-q)\Xi_r + (1-q)^2 \left(\frac{\Xi_r^2}{2} + N\Xi_r - \frac{N^3}{2} - \frac{N^2}{2} \right) \right], \quad (4.13)$$

where $\Xi_r = -N \ln \check{\beta} + 2N$. Summarizing the above expansion in the region $q \rightarrow 1$ we observe that the specific heat of the gas molecules with both translational and rotational degree of freedom may be written as the following sum:

$$C_d = C_t + C_r + M_t + M_r + M_{t,r}, \quad (4.14)$$

where the additional terms on the rhs read

$$\begin{aligned}
M_t &= (1-q)Nk \ln \left(\frac{\mathcal{V}}{\check{\beta}^{3N/2}} \right) + (1-q)^2 \frac{Nk}{2} \ln \left(\frac{\mathcal{V}}{\check{\beta}^{3N/2}} \right) \left[1 + 24N \ln \left(\frac{\mathcal{V}}{\check{\beta}^{3N/2}} \right) \right], \\
M_r &= -(1-q) \frac{3N^3k}{2} \ln \hat{\beta} + (1-q)^2 \frac{N^3k}{4} \left[3(\ln \hat{\beta})^2 - 53 \ln \hat{\beta} \right], \\
M_{t,r} &= (1-q)6N^2k + (1-q)^2 N^2k \left[\frac{315N}{8} - 2 - N^2 - \frac{15N}{4} \ln \check{\beta} \ln \hat{\beta} - \frac{5}{2} \ln \mathcal{V} \ln \hat{\beta} \right].
\end{aligned} \tag{4.15}$$

Evidently the specific heat C_d of the diatomic molecules is *not* a linear sum of the translational specific heat C_t and the rotational specific heat C_r . The additional terms owing their origin to nonextensivity may be divided into three classes. The terms M_t and M_r in (4.14) contain the effects of purely translational and purely rotational degrees of freedom, respectively. Qualitatively, these terms may be described as a kind of *nonlinear* effect of mixing of degrees of freedom. On the other hand, the term $M_{t,r}$ incorporate the effect of *both* the degrees of freedom. These cross terms indicate the existence of some sort of effective interaction between individual degrees of freedom, such as the translational and the rotational examples discussed here. These effective interactions are temperature dependent and may be thought of as induced by the nonextensive statistics. This qualitatively distinct feature is absent in Boltzmann-Gibbs statistics.

V Concluding Remarks

We have studied the specific heat of N rigid rotators in the high temperature limit. Using the disentanglement of the q exponential in an infinite product series of ordinary exponentials, we have developed a perturbative method to calculate the specific heat upto any particular order in the nonextensivity parameter $(1-q)$. This procedure is applied to find the specific heat of N rotators in the low temperature limit. Finally we calculate the specific heat of a diatomic gas with a combination of the translational and the rotational degrees of freedom. The $q \rightarrow 1$ limiting value of the specific heat specific heat leads us to conclude that there is a mixing between the different kinds of degrees of freedom due to nonextensive statistics. This mixing of independent degrees of freedom may be visualized as an effective interaction between them owing its origin due to nonextensivity of statistics. A study of these problems in the context of two parametric entropies [16,17] should be worth pursuing.

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